JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

VOL. I. No. 10.

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NEW YORK:

LEHMAIER & BRO., PRINTERS,

162 WILLIAM STREET.

1879.

Subscription Price, Five Dollars per Annum, in Advance.

THE AMERICAN CHEMICAL SOCIETY.

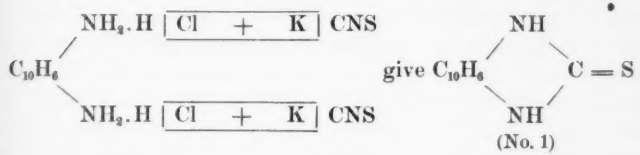
XXVII.—On a New Sulpho-Urea Compound.

By JAMES H. STEBBINS, Jr., S. B.

A short time ago, I tried to obtain a new sulpho-ureate, from naphthalenediamine and KCNS. For that purpose I proceeded in the following manner :

I dissolved 23.1 gms of naphthalenediamine hydro-chlorate, $C_{10}H_6(NH_2)_2(HCl)_2$, in as little distilled water as possible, and to this added 18.8 gms of KCNS. The mixture was stirred for a short time, and then heated for two or three hours. After the solution had cooled off, fine, long white needles made their appearance, some being as long as half an inch. These are slightly soluble in water, but quite easily soluble in alcohol.

I think the reaction may be expressed by the following terms :



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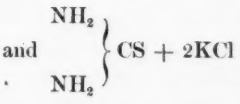
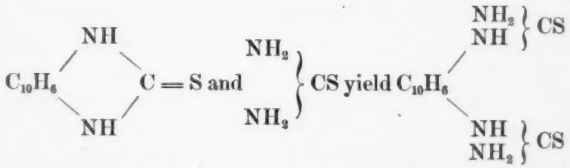


(No. 2)

Now I think that, as the reaction progresses, No. 2 reacts on No. 1, and forms a compound containing 2CS, in place of 1, viz. :



This, then, may be looked upon as a disulpho-ureate of naphthalene.

At some future opportunity, I expect to experiment on the mustard oil of this compound, which as yet has not been obtained.

XXVIII.—On Experiments with Fertilizers upon Sugar-cane, at Calumet Plantation, Bayou Téche, La.

By Prof. C. A. GOESSMANN.

It has been my pleasure, in a previous communication, to report through the Proceedings of the American Chemical Society, Vol. II., No. 2, p. 52, the results of a series of experiments with various fertilizers upon sugar-cane, at Calumet Plantation, Bayou Téche, La. The importance of the local agricultural, as well as the general industrial, interests involved in a certain solution of the object in view, have induced the progressive and public-spirited proprietor of that plantation, Daniel Thompson, Esq., Pattersonville, Parish St. Mary, La., to continue his investigations.

The original plan for the field work, which was carried out for two successive years, has been abandoned. A new course of experiments, *proposed by the writer*, at the special request of Mr. Thompson, has taken its place since the spring of 1878. The change concerns the details, and aims at a systematical application of the various fertilizing materials, for the purpose of imparting to the eventual results a better defined meaning. I had occasion to study, in previous years, the general topographical and geological features of the locality where the experiments are conducted, when visiting the Bayou Téche, for several months, as expert in connection with a scientific expedition, to inquire into its industrial and commercial resources. The physical condition of the soil on trial, as well as the nature of its constituents and latent natural resources of plant-food, I had, repeatedly, a good chance to ascertain by chemical tests. As the general character of the soil and the temporary supply of plant food, as far as the kind and the amount of each article is concerned, are known to exert, in most instances, for some time, a controlling influence on the quantity and quality of the resulting crops, under circumstances like those under consideration, I recommended a time honored and well endorsed mode of operation, which, intelligently carried out, cannot fail to secure to the careful observer, in a practical way, much valuable information—a mode which every intelligent farmer may turn to account, to some degree at least, for personal instruction in his own industry. In the making up of the compound manures, the refuse materials from Southern branches of agricultural industry, have been, for obvious reasons, in several instances, selected. Two points which the history of field experiments with fertilizers, in an unqualified manner, endorses, were beforehand conceded, namely:

the results obtained from experiments extending over a certain number of years, are alone entitled to serious consideration; and even well established results are, in most instances, essentially of local value. The general interest which a well devised series of field experiments with fertilizers may claim, consists chiefly in its educational influence, serving as a lesson for similar investigations in other localities. With these qualifications, the subsequent detailed report of Mr. Thompson's first year's work, upon the new plan, is not without some interest to those engaged in agricultural field experiments in general.

The lands engaged in the trial consist of sixteen acres in one level body. All parts of the area are equally well drained. The soil is, so far as general appearance may tell, of an uniform mechanical and chemical condition; a fine dark brown, clayish loam, rich in rooty fibres. The entire ground has been treated alike since 1863; it was left uncultivated from that year until 1871, on account of the war, and served subsequently, alternately, for the production of corn and sugar-cane. Pea-vines were raised at certain intervals for green-manuring, with the exception of 1876, when 500 pounds of cotton-seed meal, per acre, was used as a fertilizer. The entire field has been divided into sixteen plats, each one acre in size. Individual plats are separated by three rows of cane, of six feet each, making eighteen feet of unfertilized space between two adjoining plats. The canes have been harvested in the same order as the plats are numbered. The grinding began on the 9th of December, and closed on the 16th of December. One day passed by, on an average, between the cutting and the grinding of each lot of cane.

The latter were thus from twenty-four to thirty-six hours cut, before the test of the juice by the polariscope, etc., could be attended to. The season was very favorable for the cultivation of sugar-cane. In consequence of the absence of Mr. Thompson during the beginning of the grinding season, the crops of the first four plats failed to be recorded and tested, much to his displeasure. The entire experiment, I am advised, is to be repeated, in all its details, during the present season (see accompanying table).

Results of Experiments with Fertilizers upon Plant Cane at Calumet Plantation, Bayou Têche, La., 1878.

No. of Plat.	Material used as Fertilizer.	Quantity used in Pounds.	Quantity of Soluble Constituents of the Fertilizers in Pounds.	PLATS, ONE ACRE EACH. Total Cost of Fertilizers.	Per Cent. of Juice Extracted.	Weight of Cane Raised in Pounds.	No. of Gallons of Cane Juice.	Weight of the Juice in Pounds.	Density, Beaume's Saccharometer.	Density Per Cent., Saccharometer.	Result of Polariation.	Total Amount of Sugar Available in Pounds.	REMARKS.
1	Muriate of Potash.	200	Potash 167.50	$4.56	....	.....	....	.. ...	....	....	....	...	Results Lost.
2	Sulphate of Potash.	250	Potash 132.50	7.70	....	.....	..	.....	....	...	...	....	" "
3	Cotton Hull Ash...	500	Potash..... .100.00	5.00	....	.....	....	.....	....	....	....	....	" "
4	Air-Slaked Lime.. .	500	.....	2.50	...	.....	....	.....	....	....	....	....	" "
5	Gypsum.	500	....	3.60	52.2	57930	3400	30266	9.25	15.0	14.5	4386	
6	Acid Pho. Lime....	500	Pho. Acid 72.50	8.90	54.6	56030	3568	31602	9.00	14.5	12.5	3950	
7	Sulphate Ammonia.	150	Ammonia 36.00	8.25	64.0	49630	3587	31790	8.75	14 0	12.5	3974	
8	Cotton S. Hull Ash. Acid Pho. Lime....	500 500	Potash .....100.00 Pho. Acid 72.50	12.66	62.0	46780	3257	28958	9.00	15.0	13.0	3766	
9	Air Slaked Lime.... Cotton S. Hull Ash.	500 500	.. ..	7.50	61.8	42250	2937	26124	9.00	15.0	12.6	3292	
10	Cotton S. Hull Ash. Gypsum.....	500 500	....	8.60	59.9	46190	3110	27666	9.00	15.0	13.0	3497	
11	Cotton S. Hull Ash. Cotton S. Meal. ...	500 500	Potash.....110.33 Ammonia .....41.66 Pho. Acid.....18.83	10.00	61.6	56150	3898	34628	8.75	14.5	11.0	3811	
12	Cotton S. Hull Ash. Tankage.....	500 500	Potash .....100.00 Pho. Acid. ...72.00 Ammonia .. .42.00	11.00	62.2	52890	3700	32890	8.75	14.5	11.5	3815	
13	Cotton S. Hull Ash. Cotton S. Meal.... Acid Pho. Lime....	500 500 250	Potash .....110.33 Ammonia ....41.66 Pho. Acid..... .55	14.45	63.1	57670	4096	36415	8.75	14.5	10.0	3643	
14	Cotton S. Hull Ash. Tankage. ..... Acid Pho. Lime....	500 500 250	Potash .....100.00 Ammonia .....42.00 Pho. Acid ..106.00	15.45	66.0	54500	4051	35965	8.50	14.0	10.0	3595	
15	Acid Pho. Lime.... Nitrate Soda..... Sulphate Potash....	450 250 250	Pho. Acid.....65.00 Soda .....87.50 Potash ..... .162.00 Nitric Acid...38.70 Equal to Ammonia 47.11	26.60	66.2	54940	4106	36377	8.50	14.0	8.6	2513	
16	Nothing.	. ..	....	.....	57.3	39400	2511	22393	9.50	15.0	12.0	2687	

The results, although in several instances quite remarkable, are, on the whole, by no means unusual. Without any intention to enter, at this early stage of the investigation, upon a detailed discussion of the various experiments, it seems quite safe to assume, first, that *the richness of the soil* still largely controls the results; and sec-

ond, that *a different degree of maturity of the cane*, from the various plats, exerts a serious influence on the total amount of available *cane* sugar, as stated above. The last named circumstance is plainly shown by the remarkable differences noticeable in the percentage yield of the juice from the different lots of cane, varying from 52.2 to 66.2 per cent.; and also, by the not less striking differences in the composition of the juice, indicated by the results of the specific gravity test, by means of the saccharometer, which represents the relative total amount of solid matter in solution in the juice, and the tests by the polariscope, which expresses only the relative amount of cane sugar present in the latter. The actual differences in these tests are due to the presence of more or less foreign nitrogenous and non-nitrogenous substances.

As the above described experiments are instituted mainly for the purpose of finding a fertilizer which will assist in producing, upon a given area, the largest amount of cane sugar possible, and, at the same time, a cane which contains, in its juice, the highest possible percentage of cane sugar under favorable circumstances for separation, the subject of inquiry is of more than ordinary intricacy. A brief reference to experiments Nos. 5 and 13 may not be without interest in this connection. Upon these two plats the total amount of available sugar and of canes, differ in quite different proportions: for the excess of sugar exceeds that of the cane nearly three to one in favor of plat No. 5. This plat had received as fertilizer only gypsum (sulphate of lime), at a money value of $2.50 per acre; whilst No. 13 had received, what ordinarily would be designated, a complete fertilizer, containing besides a liberal amount of potassa, phosphoric acid and nitrogen, a considerable share of sulphate of lime or gypsum, the whole at a money value of $14.45 per acre. To ascribe, judging merely by the yield of sugar and cane, to the gypsum alone a higher power for aiding in the production of vegetable matter—cane sugar included—than to the combined effect of a liberal additional supply of all the essential mineral constituents of plants, as in the case of No. 13, would be in contradiction to the teachings of the best established experimental observations in agriculture. A continuation of these experiments, it may be confidently expected, will find a more satisfactory explanation in a favorable reaction of the gypsum, on either the physical condition or the chemical composition of a rich soil, or in some unsuspected combination of circumstances favorable to an early maturing of the canes.

The sugar industry of Louisiana has to contend to some considerable degree, against climatic disadvantages. The harvest of the cane has to begin at an early date, to escape the destructive influence of the frost. The planter of Cuba begins his operations frequently after the sugar season of Louisiana has closed. As the formation of the cane sugar in the sugar-cane, similar to that noticed in other sugar bearing plants, takes place largely during the last stages of its growth, it seems essential for the best success attainable in Louisiana, and similarly situated localities, to ascertain in particular the circumstances which favor an early maturity of the cane, without interfering with its normal development. Systems of cultivation as well as of fertilization, are known to exert, each in their own way, more or less influence on the duration of the period of growth. The history of the growth of the sugar-cane in Louisiana is but little known. To study systematically, by chemical and optical tests, the changes which the composition of the cane juice suffers during the advancing growth of the sugar-cane, can only increase the chances of success.

XXIX.—Contribution from the Chemical Laboratory of the Massachusetts Agricultural College.

By Prof. C. A. GOESSMANN.

SUGAR IN CORN-STALKS AND MELONS.

The examinations which form the main subject of this communication, were instituted for the purpose of testing the fitness of the juice of corn-stalks and melons, raised in our section of the country, 1876–1878, for the manufacture of sugar and syrup—an application which has been, of late, recommended. The tests were made under my direction by Mr. E. B. Bragg, a graduate of the Massachusetts Agricultural College.

1878. *Fodder Corn* (*Maize*).

Aug. 19.—Vigorous plants of Northern corn, sown for fodder upon the College farm, with the tassels just appearing, were cut off six inches above the ground, and from two to three feet of their tops, besides their entire leaf mass, removed. The remaining canes were crushed and pressed by a hand-press, to secure their juice.

Canes (fresh cut) lost moisture at 100° C. 84.82 per cent.
Canes left dry vegetable matter at 100° C. 15.18 "
Spec. gravity of juice, 5.9° Brix, at 27° C. temp.
Grape sugar in juice..... 4.35 per cent.
Cane sugar in juice..... 0.28 "

Black Mexican Sweet Corn.

Aug. 27.—The ears were just ready for the table when the juice of the canes was tested.

Canes lost moisture at 100° C..... 82.56 per cent.
Canes left dry vegetable matter at 100° C. 17.44 "
Spec. gravity of juice, 12° Brix, at 27° C. temp.
Grape sugar in juice..... 2.06 per cent.
Cane sugar in juice ..... 7.02 "

Evergreen Sweet Corn.

Aug. 28.—This variety of corn was in the same advanced state of growth as the previous one: i. e., the ears just fit for the table.

Canes lost moisture at 100° C..... 79.62 per cent.
Canes left dry vegetable matter at 100° C. 20.38 "
Specific gravity of juice, 12.7° Brix.
Grape sugar in juice..... 4.85 per cent.
Cane sugar in juice..... 5.70 "

Common Sweet Corn.

Sept. 11.—The corn was already somewhat hard when the stalks were cut to obtain the juice for examination; they had been cut a few days previous to their examination.

Specific gravity of juice, 8.7° Brix, at 26° C. temp.
Grape sugar in juice..... ... 6.6 per cent.
Cane sugar in juice..... none.

1876. *Common Yellow Musk-Melon.*

Sept. 7.—The fully ripened fruit, raised upon a sandy loam, furnished the juice for the tests.

Specific gravity of juice, 1.040, at 26° C. temp.
Grape sugar in juice..... 1.67 per cent.
Cane sugar in juice..... 2.65 "

White Flesh Water-Melon, or Ice Cream Melon.

Sept. 6.—A large and ripe specimen served for the examination.

Specific gravity of juice, 1.025, at 18° C. temp.
Grape sugar in juice..... 2.91 per cent.
Cane sugar in juice..... 2.16 "

Red Flesh Water-Melon.

Sept. 14.—A ripe fruit was tested.

Specific gravity of juice, 1.025, at 22° C. temp.
Grape sugar in juice..... 3.57 per cent.
Cane sugar in juice..... 2.18 "

Sept. 18.—A ripe fruit like the above.

Specific gravity of juice, 1.025, at 19° C. temp.
Grape sugar in juice..... 3.84 per cent.
Cane sugar in juice..... 1.77 "

Nutmeg Musk-Melon.

Sept. 11.—A full grown, yet *not ripe*, specimen gave the following results:

Specific gravity of juice, 1.030, at 19° C. temp.
Grape sugar in juice..... 3.33 per cent.
Cane sugar in juice..... 2.11 "

Sept. 12.—A *ripe* specimen of the same kind of fruit yielded a juice showing a

Specific gravity of juice, 1.050, at 20° C. temp.
Grape sugar in juice..... 2.27 per cent.
Cane sugar in juice..... 5.38 "

Sept. 11.—An *over-ripe* specimen gave the following results:

Specific gravity of juice, 1.030, at 19° C. temp.
Grape sugar in juice..... 2.50 per cent.
Cane sugar in juice..... 1.43 "

The results of the investigation leave no doubt about the question that, in our climate, neither the corn-stalks nor the melons surpass the Early Amber Cane as a source for sugar or syrup manufacture. The present condition of our sugar and molasses industry offer but little inducement to raise any of these three plants, for the production of syrup to supply the general market.

XXX.—Contribution to the Chemistry of Fruit Culture.

By Prof. C. A. GOESSMANN.

I. STRAWBERRIES.

The variety of strawberries which furnished the material for the examination, is known as the "Wilder." The plants turned to account for my tests, were raised upon the College grounds, upon a plat which, until two years previous, had been used for the production of grass. They were two years old, and in a healthy bearing condition. The first lot of fruit was just ripe when the investigation began.

One hundred parts of the entire fresh plant, without its fruit, lost 72.26 parts of moisture, at a temperature of from 100° to 110° C. One hundred parts of the ripe fruit lost from 89.03 to 90.31 parts of moisture, at a temperature of from 100° to 110° C. One hundred parts of an average specimen of our strawberry plants, before removing any of its fruit, consisted approximately of fifty-two parts of fruit, in all stages of development, and of forty-eight parts of roots, stems and leaves. One hundred parts of the fresh plant, without its fruit, left, after a careful calcination, 3.34 parts of ash constituents. One hundred parts of the ripe fruit are known to leave, according to several investigators, in the case of different *cultivated* varieties, from 0.41 to 0.63 parts of ash constituents.

A careful examination of the ashes obtained from the fruit of the "Wilder" and from the remaining portion of the plants which furnished the berries, carried out at my suggestion, by Mr. E. B. Bragg, during the past year, gave the following analytical results. The sulphuric acid and the chlorine contained in these ashes have been excluded from the calculation presented below, for the reason that the amounts noticed, even in a carefully charred mass, do not represent the exact amount present in the plant, and thus cannot serve as a basis in comparative studies like ours.

One hundred parts of the ashes, as specified previously, contained in the case of the fruits (I), and of the plants without the fruits (II):

	I.	II.	
Potassium oxide	49.24	10.62	parts.
Sodium oxide	3.23	13.35	"
Calcium oxide	13.47	36.63	"
Magnesium oxide	8.12	3.83	"
Ferric oxide	1.74	6.91	"
Phosphoric acid	18.50	14.48	"
Silicic acid (soluble in soda solution)	5.66	14.17	"

As these statements are most likely the first ones published regarding the mineral constituents of one of our prominent cultivated varieties of strawberries—the "Wilder"—it may not be without interest to fruit-growers, in general, to compare the above-stated analytical results with those of an analysis of the ashes of the fruit of the wild strawberry (*Fragaria vesca*, L), as reported by Richardson. One hundred parts of the wild fruit contained 0.41 parts of ash constituents. One hundred parts of that ash, calculated on the above specified basis, contained :

Potassium oxide	22.06 parts.
Sodium oxide	29.79 "
Calcium oxide	14.88 "
Magnesium oxide	traces.
Ferric oxide	6.07 parts.
Phosphoric acid	14.47 "
Silicic acid	12.62 "

A careful comparison of the composition of the ashes of No. 1 above, with that of the ashes of the wild fruit just represented, reveals remarkable differences, which deserve the serious attention of the practical fruit-grower; for it shows, in a striking manner, the peculiar action of these two kinds of strawberries on the soil resources of plant growth. The variations here noticeable, in regard to the relative proportions of the mineral elements in the ash of the wild and the cultivated variety of strawberries, are not less remarkable than those known regarding some of their most prominent proximate organic constituents, as sugar and acid. The ordinary wild strawberry contains usually one acid to two sugar, whilst in case of some cultivated varieties, it changes from one to six, or more.

The question, whether the variations in the relative proportions of the mineral elements found in fruits, bear any definite relation to their general character, can scarcely be any more doubted, since the study of the best modes of imparting to some of our farm crops a higher value for special industrial application, leads quite naturally to that conclusion. According to this view, it is but reasonable to consider it most important to ascertain, by careful chemical analysis, the relations which exist between the chemical and physical condition of the soil, and the mineral constituents of the fruits raised upon it ; for that kind of information furnishes the foundation of a rational system of manuring our fruit bearing plants. To produce new varieties, and to produce the best of each kind in the largest possible quantity, are questions requiring each an independent course of experimental

observation. It is quite certain that the practice of restoring to the soil—in suitable form and in due time—those constituents, at least, which the fruits we gather abstract, cannot otherwise but contribute towards large crops, by stimulating a vigorous, healthy condition of the entire plant.

A strong, healthy plant is quite naturally better qualified to overcome internal local disorders, and to resist external injurious influences than feeble specimens. The extensive root system of our fruit trees tends to conceal the gradual exhaustion of the soil ; it delays merely the failure of our orchards. A liberal supply, in particular, of those essential elements of plant food, which are found in the fruits in conspicuous quantities, and which, for obvious reasons, must serve important functions in their growth, if judiciously applied, cannot otherwise but prove beneficial to their reproduction. To secure that amount in a more defined form, *i. e.*, by means of some chemical commercial fertilizer, than has hitherto been customary, cannot otherwise but improve most decidedly our chances to ascertain not only the special wants of the plants under cultivation, but to recognize also the particular form in which the various articles of plant food exert the most beneficial influence on the quality of the fruits. I succeeded, in consequence of the liberal application of potassa and phosphoric acid, in changing the proportion of potash, and also of grape sugar, of the wild purple grape to that of a good ripe Concord grape. As the fertilizer applied had evidently modified, in a certain direction, both the organic and inorganic portion of the grapes under cultivation, the experiment can serve as an additional illustration, that the fertilization of fruits with reference to quality, is within our possibilities. The artificial feeding of fruit bearing plants, once based on rational principles, will gradually alter our current notions of severe pruning, in the interest of a larger and more valuable crop ; whilst a more thorough knowledge of the exact chemical relations of different varieties of fruit, respecting their characteristic organic and inorganic constituents, may even furnish a safer basis for the selection of varieties most promising for the production of new valuable varieties, in which well defined qualities may supplement each other.

II. CRANBERRIES (*Vaccinium macrocarpon, Gray*).

The sample of cranberries which furnished the material for my investigation, was obtained from a party engaged in their cultivation, who desired to know the relative proportion of the essential articles of plant food contained in this fruit, obviously for the purpose of

forming some definite idea regarding a successful restitution of the elements carried off by the crops. Finding no record of any previous analysis of our cranberries, within my literary resources, I decided to undertake the task of an examination to meet the request. As the results obtained with the assistance of Mr. E. B. Bragg, of the Class of 1875, may prove of interest to others, on account of the increasing importance in our own State, of the growing of cranberries, I ask leave to report them. The average specimens of cranberries tested towards the end of the month of October, in 1876 and in 1877, about two weeks after they had been harvested, contained in one hundred parts :

	1876.	1877.	
Moisture at 100° to 110° C.	89.29	89.890	parts.
Dry matter	10.71	10.110	"
Ash constituents in dry matter	——	0.179	"
Nitrogen in dry matter	——	0.160	"

The juice of these berries had in both samples, a specific gravity equal to 1.025 at 15° C. temperature. It contained in 1876, 1.35 per cent. of grape sugar, and in 1877, 1.70 per cent. of that substance. No cane sugar was found. The free acid of the juice, calculated as malic acid, amounted in the first stated instance to 2.25 per cent., and in the second one, to 2.43 per cent. It consisted most likely of two acids—citric and malic acids.

The dried ash of the cranberries collected in 1877, contained, after deducting the carbonic acid, the sulphuric acid, and the chlorine, in one hundred parts :

Potassium oxide	47.96	parts.
Sodium oxide	6.58	"
Calcium oxide	18.58	"
Magnesium oxide	6.78	"
Ferric oxide	0.66	"
Phosphoric acid	14.27	"
Silicic acid (with traces of sand)	5.22	"

In presenting these analytical results to the consideration of the cultivators of cranberries, I do not intend to recommend to them, as an unfailing receipt for the successful cultivation of that fruit, the use of a fertilizer which contains the above specified relative proportions of the various articles of plant food, compounded merely with reference to the cheapness of the form. Such a course would result ultimately in a general disappointment among practical farmers, regarding the merits of analytical chemical inquiries into the relations

of plant growth. Having, during past years, from time to time, published results of investigations of a similar character, it may not be out of place to discuss once, briefly, the question: "What do we learn from an ash analysis of plants like the above?" A good chemical analysis of a carefully prepared ash of a matured plant, is the only way by which we are enabled to ascertain with absolute certainty, the various kinds and the amount of each of the mineral elements which the plant under examination has incorporated. It is also the most exact mode by which we can learn the character, and the degree of the loss the soil has suffered in mineral matter, in consequence of assisting in the growth of that plant. Whilst we are thus compelled, in the light of our present information, to recognize a good analysis concerning the mineral constituents of all our cultivated plants, as the first requirement for the development of a rational system of manuring our farm lands, we are not less obliged to concede that we derive but a part of the information we need to insure a reasonable success under otherwise favorable circumstances. The more carefully we have studied during the past thirty years, in the field, in the vegetation house, and in the laboratory, the relations which exist between the soil conditions and plant growth, the more are we forced to recognize the correctness of that conclusion. The above stated ash analysis, like any other ash analysis of plants, gives neither any direct information regarding the particular combination, which the various constituents form within the plant, nor does it tell in what specific form the plant prefers to assimilate the mineral elements from the soil; it shows simply, that certain elements have been noticed in such quantities as stated, without claiming to give any valuable information regarding their mutual relations to each other in the vegetable economy of the plant which contains them. To recognize merely the presence of different elements in the ash of plants, does not entitle—without any other qualification—to the assumption that they are all of an equal importance, and essential for a successful growth; nor can it be asserted, with anything like certainty, that even the absolute amount of the mineral elements found in plants, is indispensable for their reproduction. The ash constituents of plants are known, as far as the same variety in a corresponding state of development is concerned, to differ in most instances more or less in regard to their absolute quantity as well as the relative proportion of their essential elements. These variations are, however, found more serious in the case of absolute quantity, amounting sometimes to from fifty to one hundred per cent. of total

ash, than in that of relative proportions. Wherever the last mentioned condition becomes conspicuous, marked differences in the relative proportion of the proximate, organic constituents of the plants will usually be found. The recent careful inquiries of Noble, Schroeder, Erdmann and others, show that the particular form in which several essential articles of plant food, as potassa, magnesia, etc., are applied for the production of crops, quite frequently exerts a decided influence on their value as far as their composition is concerned. The nature and the condition of the soil, in common with the climate and the weather, are known to exert a great influence on the preparation of plant food within the soil, and on the vital process in plant life. These and similar considerations render it quite plain that the above analytical statements concerning our samples of cranberries, however carefully secured, can have no other claim but to make known the existence of certain numerical relations among the constituents of the ash of that fruit. They are at best for general use only of an approximate character. The analysis in the connection in which it has been presented, aims at nothing else. The chemist, by carrying on the analysis of soil and plants, furnishes in the most exact way known, the proof of the existence of certain definite mutual relations between both. It remains for the agriculturist to take up the work, when the analytical chemist has, for obvious reasons, to stop; *i.e.*, he has to find out how much of each kind, and in what particular form, his soil has to receive of the essential articles of plant food, pointed out by the analysis of the chemist, to secure in an economical way, the most valuable returns from his lands. Rational and economical farming is only possible by adopting that course of operation; the safest leaders in progressive, practical agriculture point in that direction. Judging from previous observation, I should recommend, to the cultivators of cranberries, to apply the potash in the form of potassium chloride.

III. INFLUENCE OF GIRDLING THE VINES ON THE GROWTH AND THE COMPOSITION OF THE GRAPES.

In a previous communication, see PROCEEDINGS OF THE AMERICAN CHEMICAL SOCIETY, Vol. II., No. I., page 44, I described a series of experiments with grape vines, instituted (1877) for the purpose of studying the effects of girdling on the growth and composition of the grapes grown under such circumstances, as compared with those raised on the ungirdled branches of the same vine. By numerous comparative analytical tests of grapes raised under both conditions, it was proved quite conclusively that those growing on properly

girdled branches, ripened from two to three weeks earlier than those on ungirdled branches. The investigation has been directed of late, mainly to an inquiry into the circumstances which favor the production of the best and earliest ripe grapes, without endangering the life of the vines subjected to the treatment of girdling. The subsequent statement of the observation of Messrs. C. S. Howe, of the Class of 1878, and Wm. G. Lee, of the Class of 1880, upon the college vineyard, contain a summary of the results thus far secured. In entering upon these tests, it was decided to study the subject with reference to the following points :

The best time for girdling.

Width of girdle.

Place of the girdle on the vine.

Effect of girdling on the vine during the first as well as the succeeding seasons.

One hundred and ten Concord vines, located in the same part of the vineyard, of southern exposure, served for the experiment.

They were girdled at intervals of one week, beginning on the 17th of June, and closing on the 25th of August. The girdling was carried on in ten different ways. The work began with ten vines, and each succeeding week were added ten new ones to the experiment. The most suitable time for the girdling of the Concord vine extends during the entire month of July, varying somewhat, according to the more or less advanced state of general growth, due to the peculiarity of the season. The best results during the past season were obtained from vines girdled on the 7th of July, and the opening kept cleared from new growth until the middle of August, when the wound may be allowed to grow over. The girdle of one-half of an inch wide proved more efficient than those of less dimension. Larger ones are apt not to close up before the growth ceases, and thus terminate the life of the vine. Entire vines—or better, one or more years old branches of vigorous plants—are best adapted for the girdling process. The girdled new growth produced some fine fruit, and much in advance of those on ungirdled new wood ; but the liability of the latter to break, renders that mode objectionable if not wholly impracticable. The vigor of the vines remains apparently uninjured by girdling. Vines girdled two and three years ago are, as a general rule, thrifty, and although the girdle is grown over, the girdled branch produces a marked difference in its fruit ; in some instances the latter still ripens fully a week earlier.

XXXI.—Analysis of two Intestinal Calculous Concretions of Horses.

By Prof. C. A. GOESSMANN.

The material which served for the examination, was kindly furnished by Dr. N. Cressy, of Amherst, Mass.; both analyses have been carried out, under my direction, by Messrs. D. H. Benson, of the Class of 1877, and H. L. Lovell, M. A.

I.

This calculus was discharged from the bowels of a horse without any previous symptoms of disease; it measured two and one-half inches in diameter, and was round and smooth on the surface; it consisted of a hard and compact mass of numerous concentric layers, varying in color from white to bluish-white; in its fresh and dry state it weighed six ounces.

One hundred parts of air-dry calculus contained:

Ammonium-magnesium phosphate	88.01	per cent.
Calcium carbonate	0.45	"
Magnesium carbonate	5.27	"
Insoluble mineral matter (clay, sand, etc.)	0.86	"
Organic matter and moisture	5.41	"

II.

This calculus was taken from the bowels of a horse which had died in consequence of a rupture in the intestines, caused by the obstruction it produced; it measured four inches in diameter, and weighed, in its fresh, dry state, thirteen ounces; it was composed of several layers, varying in color from white to dark brown.

One hundred parts of the air-dry calculus contained:

Ammonium-magnesium phosphate	75.56	per cent.
Calcium carbonate	2.07	"
Magnesium carbonate	0.84	"
Ferric oxide	0.67	"
Insoluble mineral matter (clay, sand, etc.)	6.18	"
Organic matter (containing 1.818 per cent. of nitrogen) and moisture	14.68	"

Both concretions belong, apparently, to the same class of calculi, and differ mainly in regard to the character and the relative amount of the organic material present.

XXXII.—Some Additional Notes On Ozone.

By ALBERT R. LEEDS. Ph. D.

I.—Comparative Results Obtained with Previous Electrical Ozonisers, with Description of a Modified and Powerful Form.

In pursuing this inquiry, three objects were kept prominently in view:

1st. To obtain ozone by a method which could be relied upon at all times, and which would not only be practically independent of changes in temperature, humidity, etc., but require little or no supervision from the experimenter, after once being set in operation.

2nd. To be able both to ozonise to a maximum the air or oxygen employed, and to employ large volumes of the ozonised gas.

3rd. To render the apparatus simple and inexpensive, using the appliances at present found in a well appointed chemical laboratory.

The considerations summarized under the first head, finally caused the abandonment of a large Holtz machine, with which the experiments had been originally instituted. For, granting that by the use of suitable precautions, the disturbing influences of atmospheric variations are eliminated, there still remains the necessity of a considerable amount of mechanical power to drive the machine.

As to the second point, there was little to guide us except the results of our own comparative experiments with the various forms of ozonisers hitherto proposed, and Dr. Siemens' theoretical discussion of the principle involved in the construction of the induction tube which bears his name. In the experiments of von Babo and Claus, with an ozoniser devised by the first named, a very small volume of oxygen, confined within the apparatus, was subjected for many hours to the action of electricity, generated by a powerful coil.* The maximum degree of ozonation was reached under these circumstances, when the confined gas ceased to contract, and this maximum in various trials corresponded to 3.1 to 5.74 per cent. of ozone. Brodie employed a Siemens' tube, the interior and exterior surfaces being cooled to 0°, or even —10° by ice, or a mixture of ice and salt.†

* Researches on the Constitution of Ozone, Ann. d. Chem. u. Pharm., 140, 248.

† Sir B. C. Brodie, on the Action of Electricity on Gases, Phil. Trans., 1872, 435.

The highest percentage of oxygen obtained in this manner was 6.5 per cent. A very powerful coil was employed (how powerful is not stated), the passage of the gas in each experiment occupying about 30 minutes; and the volume of oxygen, varying from about 100 cc to less than 300 cc. Experiments were made with the view of ascertaining the effect of repeated electrization of the gas, on passing it several times through the induction tube. It was found that on its fourth or fifth passage, it contained no higher percentage of ozone than it did at the end of the first. These experiments agree, therefore, with those of von Babo and Claus, in so far as they likewise appeared to show that there was a fixed limit prescribed by the conditions of the experiments, beyond which the ozonation cannot pass, but differed in the respect that this limit was reached at once; while in von Babo and Claus, it was not obtained until after powerful electrization for many hours.

But the object in the present inquiry, was not to ozonise to a maximum, a small volume of confined gas, with the view of studying the properties of the gas itself. It was rather to ozonise to a maximum a *current* of air or oxygen, with a view of studying the reactions produced by it in the various substances with which it was brought in contact. It was also desirable, if possible, to employ a large volume of oxygen, and to keep it flowing rapidly, so that the total amount of ozone produced might be considerable. With these ends in view, the various forms of ozonisers hitherto proposed, were tried, and failed to give, in our hands, the character of results sought for, until eventually, after many modifications, a development of the Siemens' induction tube was arrived at, which has proved satisfactory.

After discarding the Holtz machine, an induction coil with a battery of 10 Bunsen elements set up as two large cells, was employed. The axis of the wheel which operated the hammer used in making and breaking connections, was also the axis of a pulley connected by a belt with another pulley, run by a small electro-magnetic machine. This latter was driven by two additional Bunsen cells, and the speed so regulated that about 60 sparks would pass between the terminals of the coil per minute. As thus arranged, the coil was used to supply the electricity employed in making the trials on the various ozonisers employed. And, without claiming that the results in each case were the best possible, yet they were the best which we could obtain, and as such are put on record, without attempting to explain why in some instances, they are so low. With these words of expla-

nation, we shall give a brief description of the ozonisers experimented upon, and their performances.

*Wright's Ozoniser.**

The first tried was that of Prof. Wright, who, however, had made use in his own experiments of a Holtz machine, as the source of electricity. The original description was followed closely. A straight glass tube, 20 cm in length and 2.5 cm diam., was closed at each end with paraffined corks, through the axis of which stout copper wires were passed, one carrying a terminal in the form of a ball, the other a terminal disc. Inlet and exit tubes were also let into the corks eccentrically, to provide for the flow of gas.

A very slow stream of perfectly dry oxygen was made to flow through the apparatus. The maximum result was 0.76 mgm of ozone per liter. The oxygen used contained about two per cent. of nitrogen. It was dried in this and the subsequent experiments, by passage through a series of sulphuric acid dryers.†

Houzeau's Ozoniser.

According to M. Houzeau's description (Compt. Rend., **74**, 256), this is constructed of a straight tube, in the interior of which is a wire of copper, lead, or better, of platinum, 40 to 60 cms long, passing through the upper side. A wire is wrapped around the exterior, which is a little longer than the interior wire, and connects with the other pole of the induction coil. With such an apparatus, and with a coil giving 2 to 3 cm sparks, Houzeau states that he readily obtained 60 to 120 mgms of ozone per liter of ozonised air, according as the experiment was performed at + 15° or — 30°. In one case he obtained 180 mgms, and expressed the opinion that the complete conversion of oxygen into ozone was to be regarded as possible.

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* Amer. Journ. Sci., 3, **4**, 29.

† NOTE.—Gianetti and Volta (Ber. d. d. chem. Gesell., **7**, 1,462), with a similar apparatus, employing the Holtz machine, obtained 15 mgms of ozone per liter. Later (ib., **9**, 84) they employed a form of Siemens' induction tube, with the inner and outer tube 2 cms and 2½ cms respectively, in connection with a Holtz machine. They found that the slower the stream, and the lower the temperature, the larger the percentage. Between 5 and 10°, ½ liter of oxygen flowing per hour, they obtained 40 mgms ozone per liter. On substituting a Ruhmkorff coil, they obtained, under like circumstances, only ⅓ this amount.

Two ozonisers of this form were made. The first, of a tube 55 cm long and 15 mm diameter. A spiral of platinum wire 90 cm long, coiled around the middle portion of the exterior of the tube, formed one pole ; a straight platinum wire passing along the axis of the interior of the tube, the other.

Result.—Oxygen used, a slow current flowing, 3.25 liters ; ozone obtained, 16.07 mgms, or 4.95 mgms per liter ; temp., 20°.

Second trial.—Oxygen used, 5.125 liters ; ozone obtained, 19.85 mgms, or 3.9 mgms per liter ; temp., 21°.

These results being highly disappointing, a more elaborate ozoniser of this class was constructed. The outside tube was 60 cm long and 18 mm diameter. Around the middle portion of this exterior tube, for a length of 40 cm, was coiled a platinum spiral, 177 cm long, with 32 turns. In the axis of this tube, another glass tube 6 mm in diameter was placed, with a similar platinum spiral, but having 70 turns, and coiled in the opposite direction. The inner tube was kept concentric with the outer by two rings of glass beads.

Result.—Placed in a mixture of ice and salt ; oxygen used, 4¼ liters ; ozone obtained, 10.03 mgms, or 4.6 mgms per liter. No better result on second trial.

Repeated.—Temp., 22° ; spark-length, 30 mm ; oxygen used, 1.6 liters ; ozone obtained, 3.78 mgms, or 2.4 mgms per liter.

Since in these and subsequent trials, Houzeau's ozoniser in my hands, yielded equally unsatisfactory results, its use was abandoned.

Boillot's Ozoniser.

Its peculiar features are : 1st. The use of gas-carbon as the material constituting the poles. 2d. The ozonised oxygen is allowed to flow through and in contact with one of these poles, instead of isolating the gas-carbon in a glass tube. The apparatus was constructed so as to embody the ideas of its author, as far as we understood them.*

The oxygen was conveyed through a glass tube, 60 cm long and 15 mm in diameter. This was closed with paraffined corks at both ends, through which smaller glass tubes were passed for inlet and outflow of gas. It was filled with coarse fragments of gas-carbon, each about the size of a pea. These were connected with one pole by a

* Compt. Rend., **75**, 214 and 1,712; Chem. News, **26**, 312; Journ. Chem. Soc. N. S., **10**, 879.

copper wire passing through the cork. The middle of this tube was surrounded by another tube 19 mm in diameter, the space between them being filled with pulverized gas-carbon, and connected by a copper wire with the other pole.

Result.—Length of spark, 60 mm at beginning, 50 mm at close of experiment; temp., 20°; time, 2 hours; amount of oxygen used, 4⅛ liters; of ozone obtained, 11.01 mgms. This is equivalent to 2.77 mgms, or 1.29 cc per liter.

*Von Babo's Ozoniser.**

The instrument of this description, as constructed by ourselves, was made as follows: 14 small thin tubes, 2.5 mm wide, and 900 mm long, were joined together two by two, and thrust into a large tube, 21 mm inside diameter, and 975 mm long. The thin tubes were kept apart by means of little pieces of tubing about 10 mm long, and just large enough to fit over the other tubes. In each tube was placed a copper wire, running through nearly its entire length, and connected with a platinum wire. They were then sealed by the gas flame. The tubes in couples were so arranged that the platinum wire of one projected from one end of the large tube, and the platinum wire of the other projected from the other end. The bundles of wire were connected at each end with copper wires going off to the coil, the junction being made outside of the enveloping tube, which was provided with an inlet and outlet for the gas.

Result.—Spark-length, 70 mm; time, 35 minutes; oxygen used, 1 liter; ozone obtained, 9.15 mgms. In the dark it was found that the discharge was not altogether silent, a few points of light being visible.

Thinking that a better result might be obtained by spreading the charge over a lesser extent, another ozoniser of this pattern was fitted up with only 5 pairs of tubes, all the other arrangements being the same.

Result.—Time, 70 minutes; oxygen used, 1 liter; ozone obtained, 2.5 mgms. Minute points of light were also noticeable in the dark, along the sides of some of these tubes.

After these trials, the attempt to employ ozonisers of Von Babo's form was abandoned.

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* "Volumetric Relations of Ozone," Ann. der Chem. u. Pharm., Suppl., **2**, 297.

*Will's Ozoniser.**

This is a Siemens' ozoniser, modified by making the inside of the inner tube a portion of a worm, through which a current of cold water is kept flowing. The object of this arrangement, it is stated (*loc. cit.*), is to prevent the heating which takes place on continued use of the Siemens' apparatus, the heating being attended with a diminution in the quantity of ozone.

We constructed an ozoniser in accordance with this description, the diameter of the exterior tube being 42 mm ; of the inner tube, 20 mm ; and the length of the opposed surfaces, where the tin pipe, forming a portion of the worm on the inside of the inner tube, was opposed to the tinfoil on the outside of the outer tube, 30 cm. But the apparatus, as we used it, did not give results of such a character as to compensate for the increased complication brought about by the introduction of a current of water. There appeared, also, to be a considerable loss of electricity from the pole connected with the stream ; and in the Siemens' ozoniser, properly constructed, there is so slight a heating of the surfaces, and so little gained from artificially cooling them (I am now speaking of the ozonation of a large volume of gas in motion, not of a small confined volume), that the employment of Will's modification was abandoned.

Siemens' Ozoniser.

The original description of this ozoniser, which was designed and constructed according to certain theoretical conceptions by W. Siemens (Ann. der Phys. u. Chem., **102**, 120), more than 20 years ago, is as follows. It is made of two tubes of the thinnest suitable glass. One of them, which is closed, and the narrower of the two, is set inside the other in such a way, that the annular space between them is of uniform width throughout. The outer is melted to the inner tube at one end, and at the other is narrowed down into an exit tube. The inlet tube is joined to the other end of the outer tube. The inner and outer surfaces of the glass tube are coated with metallic foil, and oppositely electrified.

With the objects in view, which were set forth at the beginning of this article, a very large number of ozonisers of this description were made, and the successive improvements, as shown by the increase in the amount of ozone obtained, rapidly led to the modification, which was finally adopted. The first was constructed of a tube 50 cm in length and 35 mm in diameter, narrowed down at each end so

* Chem. News, **27**, 292 ; Ber d. d. chem. Gesell., **6**, 769.

as to unite with a straight tube passing through its middle, 17 mm in diameter. The inside of this second tube was covered with tinfoil and formed one pole; the exterior of the outer tube was covered with 378 cm of tinfoil, and constituted the outer pole. The lateral inlet and exit tubes for the passage of the gas, were closed with small wash-bottles made of test tubes and containing sulphuric acid. This simple arrangement prevents backward diffusion of the ozone, and consequent destruction of the rubber connections.

Result.—Oxygen employed, 1 liter; ozone obtained, 7.18 mgms.

After the experiments given in the present article, were concluded, a Siemens' ozoniser of the pattern known as Geissler's, was received from Bonn. The interior tube was 18 mm, the exterior tube 27 mm, in diameter, and the exterior surface of the latter over a length of 30 cm, was coated with foil. About the same length of foil was contained in the inner tube. The outer tube was again surrounded by a final enveloping glass tube. All the joints and connections in this difficult piece of glass-blowing were of glass. In our own trials we were compelled to make the joints of sealing-wax and paraffine. As this lowered all the quantities found, their relative value and significance would still remain.

Result.—Spark-length, 31 mm; time, 40 minutes; oxygen used, 1 liter; ozone obtained, 28.16 mgms.

A series of experiments was now instituted to determine the influence of the extent of electrified surface, its separating distance, duration of exposure of the current of oxygen to the silent discharge, and of the spark length, upon the amount of ozone obtained. With these objects we employed:

I. Ozoniser of one meter in length, of which 850 mm were covered with tinfoil. Diameter of outer tube, 25 mm; width of annular space intervening, 1 mm; both inside and outside tubes of very thin glass.

Result.—Oxygen employed, 1 liter; ozone obtained, 23.65 mgms; spark-length, 85 mm; temp., 20°; duration of experiment, 10 minutes.

II. Length of tube, 1 meter; length of exterior of outer tube covered by tinfoil, 925 mm; diameter of outside tube, 47 mm; diameter of inside tube, 25 mm; width of the annular space intervening, 11 mm; walls of the glass tubes thicker than the preceding.

Result.—Oxygen employed, 1 liter; ozone obtained, 5.8 mgms; time, 10 minutes; temp., 22°; spark-length, 60 mm.

Therefore, in the construction of tubes subsequently made, glass tubes as thin as could be obtained, and with as small an annular space between them as possible, were employed.

III. Using the same (II.) ozoniser, an experiment was made to determine the effect of prolonged exposure to the silent discharge upon the degree of ozonation. After filling with oxygen, the coil was put into operation for 15 minutes, and then, the coil being still active, a current started and allowed to flow until 1 liter of oxygen had passed through the ozoniser, the time required being 10 minutes.

Result.—Oxygen employed, 1 liter; ozone obtained, 10.2 mgms; time, 15 + 10 = 25 minutes; temp., 22°; spark-length, 55 mm.

In this experiment, a lower result in the total amount of ozone obtained is very noticeable as compared with I., in which, however, the spark-length was 85 mm.

IV. Using, therefore, the same ozoniser (I.) with the spark-length of 55 mm, the experiment was repeated without setting the coil into action prior to beginning of the flow.

Result.—Oxygen employed, 1 liter; ozone obtained, 14.93 mgms; time, 10 minutes; temp., 25°; spark-length, 55 mm.

The foregoing experiments point out the proper directions in which to modify the apparatus, in order, under given circumstances, to bring the degree of ozonation to a maximum:

(*a.*) To diminish the distance between the electrified surfaces, both by diminishing the thickness of the glass, and by lessening the annular space between the two tubes.

(*b.*) By prolonging the interval during which the oxygen is subjected to the silent discharge. There are evidently two ways of doing this; either by lessening the rate of flow, or, the intensity of static charge being preserved the same upon each unit of electrified surface, by increasing the length of the tubes. The latter method was adopted, since the principal object in view was that of obtaining the largest possible total quantity of ozone.

(*c.*) Along with the increase in the length of the tubes, to raise correspondingly the length and number of the sparks (within the limits of the silent discharge).

(*d.*) As no notable elevation of temperature was perceived, in the case of large tubes operated in this manner, it was deemed important not to complicate the apparatus by arrangements for depressing the temperature.

Since considerable time was required to line the inside of the inner tubes with tinfoil, some trials were made to learn whether a simpler arrangement would answer.

V. The outside of the inner tube, this time of heavy glass, was

coated with tinfoil, and the outside of the inner tube with the same, the length covered by the tinfoil being 900 mm, and the annular space between the tubes 1 mm.

Result.—Spark-length, 62 mm; time, 10 minutes ; temp., 21°; oxygen used, 1 liter ; ozone obtained, 1.89.

VI. The tinfoil was transferred from the outside to the inside of the inner tube, everything else remaining the same.

Result.—Oxygen used, 1 liter ; ozone obtained, 10.58 mgms.

These trials demonstrated the importance of separating the electrified surfaces by glass walls. The tin was not noticeably affected, and the diminution of ozonation was probably due to the loss of tension consequent on removing one of the insulating surfaces.

VII. To study the effect of prolonging the interval, during which a certain volume of oxygen was subjected to ozonation, the ozoniser used in VI. was charged for 15 minutes, the gas not flowing. The volume of oxygen contained in the annular space and ozonised in this manner, was 70 cc.

Result.—Spark-length, 55 mm ; time, 15 minutes ; oxygen used, 70 cc ; ozone obtained, 2.31 mgms, corresponding to 33 mgms per liter.

Since an increase in the length of the tube would also have the effect of prolonging the duration of ozonation, the foregoing experiment suggested those which follow, and ultimately led to a satisfactory solution of the problem in hand.

VIII. A thin glass tube, 25 mm wide and 1 meter long, was coated with tinfoil over 815 mm of its outside surface. An inner tube was similarly coated on the inside over 815 mm. Its inner coating was connected by copper wire with one pole. Both ends of each tube were sealed with paraffined corks, the outer tube enclosing the inner, and the inner separated by glass rings by an annular interval of 1 mm, from the outer. A duplicate ozonising tube was prepared, and the outer surfaces of the two connected together, and with one pole of the coil, and likewise their inner surfaces with the other pole.

Result.—Spark-length, 50 mm ; temp., 21.5° ; time, 30 minutes ; oxygen used, 1 liter ; ozone obtained, 52.54 mgms.

Repeated, but the ozoniser charged for 15 minutes before beginning the flow of oxygen ; ozone obtained, 57.83 mgms.

Repeated.—The charging being begun 15 minutes before flow ; ozone obtained, 71.82 mgms.

Finding, as the result of other variations in the lengths and proportions of the tube, the conclusions arrived at above were con-

firmed, the form of ozoniser as finally used and adopted, was constructed, and will be found figured in the text. Each induction tube is a modified Siemens' tube, and may be called a Siemens' element. Six of these elements are connected together, and supported on a frame, constituting what we may term an ozonising battery. One of these frames is fitted on above another, the end elements of the two batteries being suitably connected ; and in this way, by repetition of similar parts, an ozonising tube of as great a length as desired, can be made and handled without inconvenience. Or, the electrical charge can be divided between several ozonising batteries, and the supply of oxygen, as well, so that a number of currents of ozonised gas can be used at the same time.

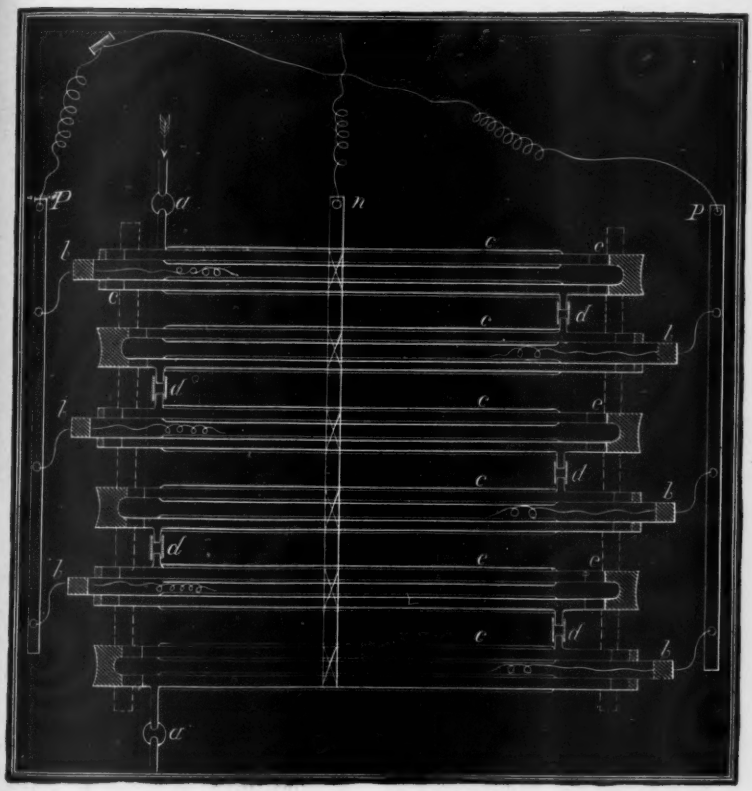
Each element is made of a tube of thin, hard glass, 60 cm long, and 21 mm inside diameter, with the inlet and outlet tubes 6 cm from each extremity. The space between these two latter tubes is coated with tinfoil. The inside tube is a little longer, one end being rounded ; the other, after the interior has been coated with tinfoil, is closed with a dry cork, through which the copper connecting wire passes. The space between the rounded end of the inner tube and the outer tube, is nearly filled by a ring of glass cut from a tube of suitable bore, and the space closed by dipping in molten sealing-wax. In coupling the elements together, the exit tube of the first is joined to the inlet tube of the second, by a wrapping of strips of muslin which are bound by flower wire, and made gas-tight by a coating of molten paraffine applied with a brush. The first inlet tube of a battery, and the last exit tube, are made parts of small sulphuric acid wash-bottles, by means of which the rubber or kerite connections, with the other parts of the apparatus, are protected from backward diffusion of the ozonised gas on the one hand, and a convenient attachment is made upon the other.

Result.—With a battery of three elements : time, 30 minutes ; oxygen used, 1 liter ; ozone obtained, 22.8 mgms.

With a battery of six elements : time, 30 minutes ; oxygen used, 1 liter ; ozone obtained, 51.74 mgms.

Repeated (after an interval, but with same number of elements).—Oxygen used, 1 liter ; ozone obtained, 49.5 mgms. With two batteries, twelve elements in all : spark-length, 45 mm ; time, 30 minutes ; temp., 24° ; oxygen used, 1 liter ; ozone obtained, 69.93 mgms.

In this shape, the apparatus proving adequate to perform the work required, it was used almost daily for three months, the average yield



DESCRIPTION.

aa Small sulphuric acid wash-bottles.
bb Corks dipped in melted sealing-wax
cc Outside coating of tinfoil.
dd Connections of paraffined cotton cloth.
ee Rings of glass.
pp Copper strips connecting with inner coatings and one pole.
n Copper strip fastened to all the outer coatings and the other pole.

of ozone, with the battery in good condition, being 72 mgms per liter, or about 5 per cent.

To obtain the best results with such a battery, the following precautions should be observed :

1st. The connection at *dd* should preferably be ground, and the other joints be made by fusion.

2d. The number of ozonising elements used should be proportioned to the strength of the coil, the maximum effect being obtained when the whole interior is luminous, but without sparks, in a darkened room.

3d. The feeble inductorium should be replaced by one giving a large number as well as a great length of sparks.

4th. The exterior foil should be covered with an outer enveloping tube of glass.

5th. The temperature of the ozonising battery should be prevented from rising, by placing it within a refrigerating chamber, and surrounding it by dry air at 0°.

II. PREPARATION OF OZONE BY CHEMICAL METHODS.

A. Potassium Dichromate and Sulphuric Acid.

According to Weltzien,* the oxygen given off when sulphuric acid is allowed to act upon potassium dichromate, contains ozone, while, according to Marignac, † it is odorless. The statement of Weltzien does not appear probable, from the fact that no evolution of oxygen takes place until the mixture is heated. But, in order to settle the question by experiment, the following arrangement was adopted: a small tubulated retort, with dropping funnel passing through the tubulure, was connected with three Geissler washing apparatus, the first of which was empty, the second and third containing water. The third Geissler apparatus was connected with a straight drying tube, in which were placed strips of moistened iodo-cadmium-starch paper. Similar strips were coiled in small open glass tubes, which were introduced into the neck of the retort. In the earlier experiments, a mixture of three parts of the dichromate (some of Merck's chemically pure) was treated with four parts of sulphuric acid at various temperatures, from the common to the boiling point of sulphuric acid. In all cases, the test-paper in the neck of the retort was turned blue, that in the drying tube remaining colorless. The wash-water retained the chlorine which had been evolved from the chlorides contained in the dichromate, and which were the source of the apparent ozone reaction.

50 gms of Merck's potassium dichromate were then subjected to 4 successive recrystallizations, and 12 gms of the salt obtained of a

* Ann. Pharm., **142**, 107; Jahresb. der Chem., 1867, 128.

† Gmelin-Kraut, Handb. der anorgan. Chem., 1872, 24.

much deeper and more brilliant red color than the original preparation. On decomposing this salt in the apparatus described above, no coloration took place in the test-papers, either before or after the passage of the evolved gases through the wash-water, or whether the experiment was conducted at ordinary or higher temperatures. No ozone, therefore, is evolved from potassium dichromate when treated with sulphuric acid, at whatever temperature the experiment is conducted, the origin of the supposed ozonic reaction being the minute amounts of chlorides which are contained in all potassium dichromate, except that which has been purified by successive recrystallizations.

B. Potassium Permanganate and Sulphuric Acid.

Similar remarks apply to the supposed generation of ozone by the action of sulphuric acid upon potassium permanganate.* In a former article,† I have shown that when the precaution is taken to conduct the experiment in an apparatus like that described in the foregoing section, the wash-waters yield the chlorine reaction, while the iodo-starch test-papers placed *after* the wash-waters, are not affected. In conducting the operation great caution is requisite, because the violet vapors of permanganic acid which are set free, are liable at any time to be decomposed with excessive violence, large volumes of oxygen being liberated and dense clouds of manganese sesquioxide formed. The least impure of a number of preparations of supposed chemically pure potassium permanganate examined, contained 97.06 per cent. of the salt, the remainder being chlorate, chloride, manganic oxide and sand.

I have called attention to this error again, because the statement that ozone is generated by the action of sulphuric acid upon potassium permanganate, is not only generally made in works upon chemistry, but because chemical manuals published subsequently to the appearance of my former note, have reiterated the statement. The error is a serious one, because medical authorities have used and still use this mixture for purifying the air of hospitals, and recently some writers on sanitary science have proposed its employment on a great scale to purify the atmosphere of places infected with yellow fever. They do so on the ground that the mixture liberates *ozone*. If, as it has been supposed, the ozone is peculiarly efficacious in the destruction of disease germs, then sanitarians must obtain it by the

* Bottger, Journ. pr. Chem., **86**, 377; Chem. News, **4**, 74; Zeitsch. f. Chem. u. Phys., **3**, 718.

† Proc. Amer. Chem. Soc., **2**, 153.

employment of other means ; if the chlorine and oxides of chlorine, which the mixture of the impure potassium permanganate usually employed with oil of vitriol, affords, are desirable, then these chlorine compounds can be more readily and cheaply obtained from other materials. We do not herein criticise the employment of potassium permanganate to oxidize putrescent and noxious organic matters, or doubt that its solution may be employed as a valuable disinfecting fluid, but desire simply to see corrected the error ingrained in works on chemistry, medicine and sanitation, that upon its admixture with an acid, ozone is given off.

C. Barium Peroxide and Sulphuric Acid.

According to the earlier publications of Houzeau,* "active oxygen" is set free by the action of concentrated sulphuric acid on barium peroxide ; but later he arrived at a different opinion, regarding the liberated gas as similar to, but not identical with, ozone.† The peculiarity consisted not in its odor, which was similar to ozone, but in its producing in contact with water, a characteristic cloud. Hence it was regarded by Schoenbein ‡ and Meissner, as their so-called *antozone*. But Nasse and Engler, § after demonstrating that the antozone which is formed when ozone is decomposed in contact with water, as is the case when ozonised oxygen is passed through potassium iodide solution, is, in fact, a chemical myth, the cloud being only hydrogen peroxide diffused through a large amount of aqueous vapor, applied the same method of investigation to the case under consideration. They passed the evolved gas through U-tubes, maintained at a temperature of 20°, and on testing the product of condensation, found that it was peroxide of hydrogen. The remainder of the escaping gas was proved to contain ozone. We have repeated their work under a variety of conditions, but have nothing to add further than some determinations of the influence of temperature upon the amount of ozone generated, and a remark upon the availability of the method for any practical use.

In an experiment in which 20 gms of barium peroxide hydrate were decomposed by sulphuric acid added in small portions at a time, the retort being surrounded by ice, and the operation continued for

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* Compt. Rend., **41**, 947.

† *Ib.*, Feb. 21, 1870.

‡ Journ. für prakt. Chem., **83**, 86.

§ Ann. der Chem. u. Pharm., **154**, 230.

30 hours, 14.29 mgms of ozone were given off. On replacing the potassium iodide solution used to absorb the ozone, by a fresh solution, and continuing the operation at the same temperature for 6 hours longer, only 0.04 mgm of ozone additional was given off. In these and the following experiments, six wash-bottles were interposed to absorb the last traces of hydrogen peroxide.

A second experiment conducted at 27°, the amount of barium peroxide being 15 gms. and the time likewise 30 hours, the amount of evolved ozone was 7.41 mgms. A final trial at 50°, with same amount of material and of equal duration, yielded but 3.88 mgms of ozone.

These results show, in a striking manner, the rapid decrease in the production of ozone with elevation of temperature, and they likewise make evident, that while we have in this purely chemical process an indubitable source of ozone, yet the amounts obtained under the most favorable circumstances are so small, that the process unfortunately cannot be utilized to any practical end.

III. HYDROGEN PEROXIDE AND SULPHURIC ACID.

That the oxygen given off on the decomposition of hydrogen peroxide by strong sulphuric acid contained ozone, was originally stated by A. Riche,* a result abundantly confirmed by our trials with the same apparatus, as that used in the experiments with barium peroxide. Since in the latter case, the evolution was greatest at the lowest temperature, the retort containing the hydrogen peroxide was surrounded by ice. The evolved gas, after repeated washing, turned not only the various iodo-ozonoscopes and Houzeau's test blue, but changed guaiacum tincture, and blackened moist silver foil as well. The same tests, I should have stated, were likewise at once affected by the ozoniferous oxygen evolved from the mixture of barium peroxide and sulphuric acid.

IV. NON-PRODUCTION OF OZONE IN THE CRYSTALLIZATION OF IODIC ACID.

It has been stated by Prof. H. H. Croft,† that air over crystallizing iodic acid becomes ozonised. In preparing the acid according to Millon's process, Prof. Croft noticed that when the acid was left

* Bull. Soc. Chim., 1860, 178.

† Chem. News, 25, 87; Amer. Journ. Sci., 3, 466; Canadian Journ., 13, No. 3.

to crystallize over oil of vitriol, the air in the jar (over the drying dish) had the characteristic odor and gave the usual tests of ozone. He states that the solution in every instance, was boiled down to thin syrup, so that no trace of chlorine or nitric acid could possibly have remained. The air in the jar was tested from day to day, both by the smell and the action upon iodized starch paper. Even when a few crystals began to form, no change was noticed, but when the crystallization set in fully, the evolution was most remarkable, the strong smell being quite characteristic, entirely different from that of chlorine or nitric acid.

We have repeated these experiments, and have found that the phenomena may be quite differently interpreted. After preparing the potassium iodate, by oxidation of iodine, by means of potassium chlorate and nitric acid, and expulsion, as far as possible, of free chlorine from the solution, the potassium was converted into the barium salt, and the latter washed thoroughly. This was then decomposed by an equivalent weight of sulphuric acid, and after separation from the insoluble salt, the solution of iodic acid was evaporated nearly to the point of crystallization. It was then transferred to the apparatus used in the experiments on potassium dichromate, barium peroxide, etc. The dropping funnel was now, however, replaced by a tube through which a very slow current of dessicated air was continuously aspirated. The test-papers in the space above the iodic acid turned blue even before crystallization set in. At the end of 6 hours they began to bleach, and at the expiration of 24 hours had become colorless. The test-papers exposed to the current, after its washing through the small amount of water contained in the Geissler bulbs, remained colorless throughout this and all succeeding trials. The strong odor given off from the crystallizing solution, was compared from time to time with the ozone generated by an electrical ozoniser, and was found to be essentially different in character. The crystallized iodic acid was then redissolved in the smallest possible amount of water, and recrystallized in the same manner. The test-papers were less and less affected at each recrystallization, until finally no change whatever occurred in them, either in the process of evaporation or in the act of crystallizing. The crystals were nearly colorless, with brilliant faces of considerable size. Now, when the difficulty of getting rid of every trace of extraneous matter by chemical operations, however carefully conducted, is borne in mind, it appears to me that the simplest explanation of the above phenomena is, that the apparent ozone reaction is not due to ozone produced in the act of

crystallizing, which, as Prof. Croft says, is anomalous, but to a trace of chlorine or nitrous acid, or possibly some lower oxide of iodine formed in the process of manufacture, and gradually eliminated by successive recrystallizations of the acid.

V. ACTION OF OZONE UPON ORGANIC SUBSTANCES.

The principal portion of our knowledge upon this subject is derived from the extended investigations of Gorup-Besanez.* He found, as might be anticipated, that the action of ozone upon organic bodies, was far more powerful in the presence of alkalies than in their absence. In the latter case, most of the substances operated on were unaltered, as urea, alloxan, allantoin, leucin, amygdalin, cane and grape sugar, inosite, mannite, glycerine, olein, starch, fibrine, glutin, hippuric acid, purified galls, and also the organic acids free from nitrogen, like acetic, butyric, palmitic, lactic, oxalic, tartaric, malic and citric. But in the presence of alkalies, in these and other cases, a powerful action took place: urea was decomposed, with evolution of carbonic acid and ammonia; leucin yielded ammonia and valeraldehyde ; grape sugar was completely oxidized to formic and carbonic acids, as was also, although less readily, cane sugar. Volatile, fatty acids were likewise oxidized in presence of alkalies, formic acid yielding carbonic acid, acetic yielding carbonic and formic acids, and butyric acid the same. Non-volatile, fatty acids were but little affected, a small amount of carbonic acid being given off after prolonged action.

It appeared probable after the construction of an ozoniser, which renders it possible to employ large amounts of strongly ozonised oxygen (72 mgms per liter), that interesting results might be obtained by the ozonation of organic compounds. Many of the bodies experimented upon by Gorup-Besanez were, therefore, studied anew, but little was done beyond confirming his original results. The complex molecules of organic structure are broken down under the destructive action of so powerful an oxidant, and rearrange themselves either into familiar bodies belonging to simpler types, or the carbon and hydrogen atoms are eliminated in the form of carbonic acid, water and hydrogen peroxide. Absolute alcohol, for example, surrounded by ice, yields on ozonation, large volumes of carbonic acid, and formic acid, acetic acid, aldehyde and hydrogen peroxide,

* Ann. der Chem. u. Pharm., **118**, 232, and **125**, 207.

are left behind in the liquid. According to A. Boillot,* there is likewise formed a white powder, which is deposited on the evaporation of the residue in the air, and which is soluble in water and alcohol. This singular product, whatever it may be, we did not succeed in procuring. According to Gorup-Besanez, glycerine yields on ozonation in alkaline solution, carbonic, formic, propionic acids, and possibly also acrolein. In addition, we found that considerable amounts of hydrogen peroxide were formed, as well. In fact, the preparation of hydrogen peroxide by the ozonation of suitable organic bodies, may possibly afford a method of obtaining this difficultly obtainable body, more convenient than those at present in use.

New Test for Hydrogen Peroxide: In testing for hydrogen peroxide, an aqueous solution of *diastase* was used in place of malt extract. The reaction is a delicate one, and the diastase solution remains unchanged for a long time.

Ozonation of Petroleum and of Petroleum Products.

The object of this inquiry was to discover what changes could be produced in petroleum, or in the distillates from petroleum, by means of ozone, which would so alter the color, odor, volatility, inflammability or other properties, as to render the process of ozonation of importance in the arts. The hope was also entertained that bodies of definite physical character, and susceptible of crystallization, would be isolated, which would serve as starting points of interesting chemical studies.

As a preliminary experiment, some crude petroleum from the carboniferous strata of Ritchie Co., W. Virginia, of specific gravity 0.885, was treated for 17 hours with the air ozonised by the phosphorus ozonator. Its dark green color at the expiration of this interval had grown somewhat lighter, and it appeared to burn less readily. It was then connected with the electrical ozoniser, and subjected to the action of a slow current of ozonised oxygen for 5 days. The liquid portion was then poured off from the yellowish-white residue, which was afterwards dissolved in alcohol. It dissolved readily, but refused to crystallize on standing. On combination with soda, and separation from the soda salt by addition of a mineral acid, the same thick, uncrystallizable oily substance was obtained.

Another preliminary experiment was tried upon a petroleum distillate which had been preserved, exposed to diffused light in a cork-

* Chem. News, **27**, 256 ; Compt. Rend., May 5, 1873.

stoppered bottle, for 6 years. During this interval considerable sediment had been deposited, and the oil which was originally nearly colorless, had assumed a strong reddish hue. Before ozonation of the oil its specific gravity was 48° B., its flashing point 88° F., its burning point 93° F.; after being treated with ozonised air for 12 hours these numbers were respectively 45° B., 96° F., and 123° F. Another distillate of specific gravity 51.5° B., flashing point 100.4° F., burning point 127.4° F., after similar treatment, afforded instead of the foregoing, the following results: 49.4° B., 102.2° F., and 128.3° F.

It would at first sight appear that the effect of ozonation had been to increase the specific gravity, and notably to diminish the volatility and inflammability of the petroleum distillate—results of great practical value. But it must be remembered that the volume of ozone obtained by this method of phosphorus ozonation, is but small compared with the total volume of air drawn over, about 1 cc per liter, so that similar effects might have been obtained by aspiration through the oil, of air alone. Subsequent experiments with non-ozonised air showed that this was actually the case.

A series of six petroleum distillates were then kindly furnished to the author by Mr. A. Bourgougnon, who had obtained them according to the method which he has described in the JOURNAL OF THE AMER. CHEM. SOCIETY, I, 188. They were derived from one sample of crude petroleum, and were as follows:

	PER CENTS.	TEMPERATURES [C.]	SPECIFIC GRAVITIES [15° C.]
No. I.	0 p.c. to 8 p.c.	124° to 142°	0.707 to 0.728
" II.	8 p.c. to 16 p.c.	142° to 163°	0.728 to 0.746
" III.	16 p.c. to 24 p.c.	163° to 186°	0.746 to 0.758
" IV.	24 p.c. to 32 p.c.	186° to 209°	0.758 to 0.772
" V.	32 p.c. to 39 p.c.	209° to 238°	0.772 to 0.785
" VI.	39 p.c. to 50 p.c.	238° to 283°	0.785 to 0.808

The first experiment was made with distillate No. VI., a determination of the specific gravity of which, as made by ourselves with the pycnometer, showed 0.789 at 15° C. 30 cc of this oil were treated for 80 hours with oxygen strongly ozonised by the 12-tube electrical ozoniser. At the end of this time, the oil was allowed to stand, when a heavy, yellowish, oily body subsided, which was separated mechanically from the rest of the liquid as far as possible, and left for several days to ascertain whether it would crystallize. But it would neither crystallize of itself, nor from its solutions in alcohol, ether,

carbon disulphide, chloroform or benzole, in all of which it is freely soluble. After these various treatments, it still retained its original strongly acid reaction. It was then converted into a soda salt, which was likewise uncrystallizable, and from this, again, separated by a mineral acid. But the oil so obtained preserved its original characteristics, nor did it crystallize after solution in the different solvents enumerated above. The specific gravity of the mixture of the oil and the acid product was 0.798; the density of the latter in an unmixed condition could not be successfully ascertained. Since it was found by another experiment that the density of a volume of oil equal to that used in the preceding experiment, was altered to 0.7967 by the aspiration of 100 liters of air through it, the change in density was mainly attributable to the removal of some of the more volatile constituents, and not to the action of ozone.

No. V. was then treated in the same way, and for the same length of time, 30 cc of the oil being used, and 125 liters of ozonised oxygen passed through it. When removed from the ozoniser, it manifested precisely the same characteristics as the foregoing, a heavy oil of a strongly acid reaction subsiding. But neither it, nor its soda salt, in their original condition, or after solution in various solvents, were obtained in a crystalline form.

Oil No. V. was then ozonised after mixture with caustic soda. At the close of the operation, the same heavy acid oil was separated by addition of a mineral acid, and on treatment with different solvents, behaved like the foregoing.

Finally, to determine whether all the various distillates would prove equally unsatisfactory or no, a sample of oil No. II., which contained the more volatile portions, was ozonised. As similar results were obtained, the experiments were abandoned. In all these trials, the vessel containing the oil was surrounded with ice during the process of ozonation.

VI. ON THE ACTION OF OZONE ON CARBONIC OXIDE.

A variety of considerations render it probable that ozone would act upon carbonic oxide, and raise the compound to the highest possible stage of oxidation. These considerations, and the important theoretical questions whose solutions would be affected by a positive result in the experiment, have recently been summarized in an article bearing the above title, by Professors Remsen and Southworth.* In repeating their experiments which, most unexpectedly to them, yielded

*Am. Journ. Sci., 3, 11, 136.

a decided and emphatic conclusion *in the negative,* I have not been influenced by any doubt as to the accuracy of their investigations, which were carried on with elaborate precautions and repeatedly verified, but I believed that long continued experimentation had put in my hands a method of procuring large volumes of oxygen, raised to a higher degree of ozonation than the ozonised gas hitherto employed, and I thought that the theoretic importance of the subject, warranted the institution of a fresh attempt to discover whether, with ozone of this character, no oxidation of carbon monoxide occured. Moreover, certain preliminary experiments had shown that carbonic oxide might undergo conversion into carbonic acid, under the same circumstances which brought about the oxidation of the oxygen molecule to the state of ozone. These were notably two : 1st. The oxidation of carbonic oxide by air over moist phosphorus at ordinary temperature, an account of which experiments, resulting in one case in the production of 14 mgms of carbonic acid, has already been published.* 2d. The simultaneous formation of carbonic acid and ozone, in a mixture of carbonic oxide and oxygen subjected to the influence of the silent electrical discharge. The carbonic oxide was washed through a series of wash-bottles containing water, caustic potash and baryta water, in the process of preparation. It was similarly washed in its transfer from the gas-holder to the gasometer, the last bottle, containing baryta water, in this case remaining pellucid. The same precaution was observed in its passage to the ozonising battery, where it was mingled with as nearly as possible an equal volume of oxygen purified in like manner, and caused to flow through the apparatus at the same rate. Two liters of the mixed gases were allowed to pass through per hour. The escaping gases were made to flow through a Geissler bulb containing baryta water, which in the final experiment was weighed, and provided with a calcium chloride guard tube, likewise weighed, before beginning of the experiment. After obtaining in several preliminary trials an abundant precipitate of barium carbonate, a quantitative determination was made with the result of showing, that after 1½ liters of carbonic oxide had been subjected in this manner to the influence of the silent discharge, in company with oxygen, 0.0271 mgms of carbonic acid had been formed.

Finally, the oxygen ozonised as in the preceding experiment to the extent of 72 mgms per liter, was mingled in excess with the carbonic oxide in a tube 1 meter in length, placed *beyond* the ozoniser. In this experiment, a very slow current flowing and continued for

* Journ. Am. Chem. Soc., 1, 232.

many hours, no change whatever took place in the baryta water. In other words, oxygen containing a very large percentage of free ozone, is not capable of effecting the oxidation of carbonic oxide.

In this case, the energy of combination of the two bonds, presumably free, of the carbon monoxide molecule, appears to be of less valency than the energy with which any one atom in the ozone molecule, is retained by the other two. In the two former instances, the ozone molecules are in the process of formation, and in the pre-existent stage (in which the oxygen molecule undergoes a dissociation), the liberated oxygen atom is seized upon by the unsaturated carbonic oxide.

VII. REDUCTION OF CARBONIC ACID BY PHOSPHORUS AT ORDINARY TEMPERATURES—CORRECTION OF AN ERRATUM.

In a former communication with this title, I have stated that when moist phosphorus is allowed to act upon carbonic acid at ordinary temperatures, a reduction occurs with the formation of a small amount of carbonic oxide. Moreover, that a notable amount of hydrogen phosphide is formed at the same time. On repeating the experiments, the latter statement was confirmed, but the former proves to be erroneous. The fact that hydrogen phosphide is given off, was not discovered until the first series of experiments, in which the products of the reaction were aspirated through solutions of palladium chloride, was completed. And then, while pains were taken to discover that carbonic oxide is entirely without action upon argentic nitrate, the salt employed to absorb the hydrogen phosphide, the reducing action of the latter upon the palladium solution was overlooked. In repeating the experiment, 13 sticks of phosphorus were placed in a 9-liter bottle, and partly covered with water. The bottle was then filled with carbonic acid, free from air, and after sealing, exposed to the sun-light for four days. Afterwards, the contents of the flask were aspirated through solutions of potassium iodide, argentic nitrate and palladium chloride. The first and last were unaffected; the silver solution contained a dense precipitate. The metallic silver in this precipitate amounted to 0.178 gm. The same results were obtained in diffused light, but in much smaller amount. On passing large amounts of carbonic oxide through a silver solution, no change occurred, showing that the result obtained above was entirely due to hydrogen phosphide.

My thanks are due to my assistant, Dr. Edgar Everhart, for his aid in the performance of these experiments.

Reports on Special Departments of Chemical Science.

On the Density of Chlorine at High Temperatures.

Note by Ad. Lieben (Comptes Rendus, No. 6, August 11, 1879.)
Translated by A. Bourgougnon.

Messrs. Victor and Carl Meyer, in following up the very important researches of Victor Meyer, on the densities of vapors, have recently (Berl. Ber., 1879, p. 1,426) attained a result of extraordinary importance. They have found that at temperatures ranging from 1,240° to 1,567° C., the density of chlorine (air being unity) is not 2.45, as is the case from 0° to about 600° C., but only 1.63. Their conclusion is that the molecular weight of chlorine at such high temperatures is not 71, but 47.3. This number not being a multiple of the generally accepted atomic weight, Cl = 35.5, the authors have inferred that chlorine may, perhaps, not be an element, but a compound of oxygen, such as has been assumed in the old murium hypothesis, or that, if chlorine be an elementary substance, the atom, Cl = 35.5, is, itself, composed of smaller atoms, *i. e.*, Cl = $\frac{1}{3}$ Cl = 11.83. The change of density from 2.45 to 1.63, and of molecular weight from 71 to 47.3, which takes place at high temperatures, will then be, to a certain extent, similar to the well known change undergone by the vapor of sulphur under similar conditions. Nevertheless, the very essential difference is noted, that the change in the density of sulphur vapor may be explained as the result of a new arrangement of the atoms, while, in the case of chlorine, it would be necessary to halve the atom, and even to admit the existence of new, and smaller, atoms, a proceeding which is not warranted by any known facts.

Even if we admit, with V. and C. Meyer, that all errors have been avoided in their experiments, and especially, that the porcelain of the vessels, and the platinum, did not evolve any trace of gas under the conditions obtaining therein, the facts observed by them are nevertheless susceptible of another interpretation than the one they have given. This note has, indeed, no other object than to direct attention to this point, and to provoke more decisive experiments. A considerable number of volatile compounds of chlorine are known, and there has never been found in their molecules, as determined by the vapor density, a smaller quantity of chlorine than that which is to-day considered as an atom, and which weighs 35.5 times as much as one atom of hydrogen. There has never been found in the mole-

cules of chlorine compounds any quantity of chlorine which was not a multiple of 35.5. The greater the number of chlorine compounds studied, the less becomes the probability that the value that we call one atom (Cl = 35.5) can be divided into smaller atoms.

The interesting fact, observed by V. and C. Meyer, that the density of chlorine, compared with air, decreases with the elevation of temperature until it becomes two-thirds of the ordinary density, may, however, be brought into accord with the generally accepted atomic weight, and even the molecular weight of chlorine. It is, for this purpose, simply necessary to assume that chlorine, after reaching a temperature of 700° C., follows a different law of dilation from other gases, *i. e.*, that its coefficient of expansion is somewhat greater than those of oxygen, nitrogen, gaseous sulphur and gaseous mercury, the densities of which have been determined by the Messrs. Meyer at high temperatures.

We know that gases under high pressure do not follow Marriotte's law, and that the compressibility varies according to the nature of the gas. Thus, under a pressure of 2,790 atm., it is not possible, according to Natterer, to compress 2,790 vols. of hydrogen, but only 1,008 vols., into the space filled by 1 vol. under the pressure of 1 atm. In the case of nitrogen, the same space cannot contain, under a pressure of 2,790 atm., 2,790 vols., nor even 1,008 vols., but only 705 vols. The two gases evidently did not follow Marriotte's law, and hence, show a different degree of compressibility.

We do not know exactly what the coefficients of expansion of the different gases are, at temperatures of from 1,200° to 1,600°; it may be that they diminish, but it is not irrational to assume that the coefficient of dilation of chlorine may be greater than that of nitrogen and oxygen, and that, at temperatures below 600° C., the coefficients of dilation of the three gases may appear sensibly the same. The consequence would be, that the density of chlorine, compared with nitrogen or air, would be smaller at from 1,200° to 1,600° C., than at from 0° to 630° C.

There is yet another explanation for the decreased density of chlorine. We may imagine that the molecules of chlorine (Cl_2) undergo, at high temperatures, a veritable dissociation into isolated atoms. If that dissociation be complete, the density of chlorine would become one-half (1.23) of the ordinary density. Now it is possible that, within a certain interval of temperature, the dissociation is left incomplete, that the molecules are decomposed into atoms, and that these isolated atoms combine again to regenerate the molecules

Cl_2. There might thus result a kind of equilibrium of such nature that half of the molecules are decomposed into isolated atoms, and, consequently, that the density of the gas becomes two-thirds of the normal density of the non-dissociated molecules Cl_2.

I very willingly admit that the two explanations I have given of the facts observed by the Messrs. Meyer, are not demonstrated, and may give rise to objections, but it seems to me that they are more easy to admit than a new atomic weight for chlorine which would be in contradiction with the definition of the atom, *i. e.*, the smallest quantity of an element contained in the molecules of its compounds.

Report on Foreign and American Patents relating to Chemistry.

Foreign Patents.

Condensed from R. BIEDERMANN'S Report to the German Chemical Society, by H. ENDEMANN.

CHARLES NORRINGTON, Plymouth : (Engl. P., No. 4139, Oct. 17, 1878.)—*Prevents loss of sulphurous acid from pyrites furnaces* during the process of recharging, by having the ash-pits closed with air-tight fitting sliding doors, which close automatically when the furnace is opened above to be recharged.

JAMES COCHRAN STEVENSON, South Shields : *Apparatus for the manufacture of soda.* (Engl. P., No. 4148, Oct. 18, 1878.)—Relates to an improvement in the construction of evaporating pans.

EDW. W. PARNELL, Liverpool : *Improvements in the manufacture of alkali.* (Engl. P., No. 4188, Oct. 21, 1878.)—The improvement consists in the use of zinc for the removal of sulphides, sulphites and hyposulphites, all furnishing zinc sulphide. Any zinc which might have gone into solution, is removed by untreated lye. Instead of using zinc, a solution of oxide of zinc in caustic alkali may be used; this, however, removes only the sulphides. The zinc sulphide is, for the purpose of regenerating zinc oxide, mixed with zinc sulphate and calcined.

FRANKE CLARKE HILLS, Deptford : *Improvement in the manufacture of ammonium sulphate.* (Engl. P., No. 3257, Aug. 17, 1878.)—Relates to an arrangement of communicating saturating tanks.

JEROME NARCISSE JOUVEAU DUBREUIL, Paris : *Method for the manufacture of iodine and bromine and other valuable substances, from varek.* (Germ. P., No. 6896, Jan. 9th, 1879.)—The plants are first reduced in machines similar to those used for the manufacture of wood paper pulp. The mass thus obtained, is then mixed with four or more per cent. of lime, and left standing for 12 hours. The sap is then separated from the insoluble part by means of an hydraulic press. Thus 1000 kgs of plants yield 800 pounds solution and about 200 kgs of yet moist pulp. This is washed with water, which is used for the slacking of new portions of quick lime. The quantity of iodine which may be obtained depends

upon the nature of the plants, those which are collected from the bottom of the sea yielding most. The pulp containing the lime is said to be useful as a fertilizer.

J. H. C. BEHNEKE, B., Billwärder : *Alumina and alkaline carbonates from bauxite.* (Germ. P., No. 7256, April 1, 1879.)

PAUL PICCARD, Lausanne : *Concentration of brine.* (Eng. P., No. 3109, August 6, 1878.)

JUL. WILH. KLINGHAMMER, Braunschweig : *Apparatus to saturate solutions with sulphurous acid.* (Germ. P., No. 6389, Dec. 20, 1878.)—Uses simply a tower, into which the sulphurous acid, which is prepared by the combustion of sulphur, is introduced at the lower end.

JOS. TSCHERNIAC and H. GUENZBURG, Paris : *Improvements in the apparatus used for the synthetic preparation of sulpho and ferro-cyanides.* This is an addition to the Germ. P., No. 3199. (Germ. P., No. 7079, April 16, 1879.)—Ammonium sulpho-cyanide is produced in an enameled kettle, which is heated by a steam coil laying in the bottom. This kettle is connected with a similar one above, which is kept cool by a coil through which cold water is passed. During the operation a constant boiling of bisulphide of carbon takes place, which is cooled above and thence conducted back into the first. For the reduction of the iron sesquioxide to iron, a furnace consisting of several parts, one above the other, is applied, in which the mixture of oxide and carbon is gradually passed towards the hottest part of the flame. The reducediron is received in a chamber from which the air is excluded.

E. A. PARNELL, Swansea : *Produces zinc oxide by heating the sulphate with carbon, or substances containing carbon.* (Engl. P., No. 3237, Aug 16, 1878.)

CL. ED. MANGIN-LESUR, Paris : (Germ. P., No. 7498, April 16, 1879.)—*Looking-glasses* are prepared by first silvering the glass; upon this, a solution of mercurium potassium cyanide is then brought, which is decomposed by zinc dust dusted over it.

ELIZABETH JANE CORBETT, San Francisco : (Engl. P., No. 2213, June 3, 1878.)—*Conducts sewer gas, for the purpose of disinfection,* through lamp-posts into the interior of street lanterns.

G. KUEHNEMANN, Dresden : *Method for the separation of the constituents of grain.* (Germ. P., No. 7056, Feb. 22, 1879.)

G. J. VEDOVA, Smyrna : (Engl. P.)—*Preparation of a powder or extract containing tannic acid,* from certain excrescences of oak trees in the Levant.

E. SCHRADER and O. DUMCKE, Koenigsberg : *Method and apparatus to melt amber and gum copal under exclusion of air.* (Germ. P., No. 6322, Jan. 19, 1879.)—From the slightly inclined apparatus which, at its lower end has a stop-cock, the air is expelled by indifferent gases or steam. The darkening of copal is thus prevented.

C. SCHEIBLER : *Improvements on the apparatus used for the experimental extraction of sugar-beets.* (Germ. P., No. 7493, April 29, 1879.)

D. ROBERTSON GARDNER, Glasgow : *Preservation of wood.* (Engl. P., No. 3261, Aug. 19. 1878.)—The wood is first treated with neutral, alkaline and acid vapors, and freed from the sap. It is finally impregnated with mercuric nitrate or other substances.

GUSTAV BERNHEIM, Brussels : *Fire extinguisher.* (Engl. P., No. 4089, Oct. 29, 1878.)—Consisting in 1000 pts, of 700 calcium chloride solution, 44° B., 20 conc. solution of borax, 29 potassium bicarbonate, 90 conc. solution of sodium tungstate, 90 ammonium chloride solution, 160 sodium chloride solution, 29 magnesium sulphate solution and 79 water. Nothing is said of what becomes of the various precipitates. The material is kept in barrels, and used in case of fire, in the place of water.

SAM. ARTHUR PETO, London : *Graphite crucibles.* (Engl. P., No. 3992, Oct. 9, 1878.)—Black lead crucibles absorb water to a considerable extent, and before use they must be carefully heated. To prevent the absorption of moisture, and the cracking by careless heating, the inventor covers the crucibles with a mass consisting of 12 clay, 2 Cornish stone, 4 burnt clay and ½ manganese. The crucible thus covered, is then heated in a stove. Some salt thrown into the stove improves the glaze, which is said to correspond well in its coefficient of expansion, with the mass of the crucible, thus preventing that it cracks or loosens during cooling.

PHIL. EMBURY LOCKWOOD, London : *Medicine.* (Engl. P., No. 4192, Oct. 21, 1878.)—Mixture of cod liver oil and malt extract.

American Patents.

Condensed from the Official Gazette of the **U. S. Patent Office,** by ARNO BEHR.

October 7, 1879.

220,304.—*Explosive compounds.* JOHN PATTISON.

An explosive compound, having for its base chlorate of potassium, is mixed with a certain proportion of coarsely ground mustard, or flax-seed. This addition is intended to prevent premature and spontaneous explosion.

220,321.—*Artificial fuel.* EBENEZER BURGESS WARREN.

A mixture of coal tar, pitch and petroleum tar, or wax-tailings with coal-dust, as obtained at the mines.

220,334.—*Varnishes.* REVERE M. BREINIG.

The varnish is made of metalline gum, caustic soda, or potash, resinous gum, linseed oil, chloride of sodium, turpentine, and a drier consisting of a metallic salt.

220,397.—*Manufacture of chloroform and allied products.* JOHN W. MALLET.

Brief : This improvement consists in forming from the vapors and gases arising from petroleum springs, or from the light products of distillation of petroleum, chlorine substitution products, by bringing the chlorine into close contact with such hydro-carbons through the intervention of a porous substance, or of metallic chlorides, and by separating such products from each other by fractional distillation.

220,449.—*Manufacture of chloride of zinc.* WM. H. WAHL and EDWARD Y. ETTENHEAD.

The inventors obtain a crude commercial chloride of zinc, by treating with hydrochloric acid the alloy of zinc and iron formed in the manufacture of galvanized iron.

Reissue 8,921 of patent 162,394.—*Processes of reducing asphaltum to a liquid.* ARCHIBALD K. LEE.

A by-product from the redistillation of spirits of turpentine, is mixed with the asphaltum in the cold, and keeps it in a fluid state ready for use for paving, roofing, etc.

October 14, 1879.

220,499.—*Carboys.* FREDERICK W. SEYMOUR and EDWARD THOMAS.

A carboy has two trunnions attached to its sides by which it hangs, and around which it swings within a side-frame.

220,532.—*Process of treating non-feltable animal hair.* GIDEON HAMILTON.

It is claimed that such hair, after treatment with a fixed caustic alkali, or lime, can be used for felting, spinning, and for mattresses and upholstery.

220,533.—*Treatment of animal hair.* GIDEON HAMILTON.

The treatment consists of boiling the hair in an acid solution first, and then immersing it in an alkaline solution.

220,534.—*Blasting powder.* ORLANDO B. HARDY.

Nitrate of soda, sugar, salt, charcoal, sulphur and paraffine.

220,539.—*Vinegar apparatus.* SAMUEL LEVY.

Brief: Modification of "Singer's essig-generator" by the introduction of a perforated diaphragm, whose upper surface is in a plane with the bottom of the lateral perforations in the descent pipes.

220,638.—*Compound dyes.* GUSTAV MOLT.

A mixture of indigo, soda, tin-crystals and syrup, making a merchantable indigo dye, ready for immediate use.

220,686.—*Filter presses.* ALBERT WEGELIN.

October 21, 1879.

220,708.—*Methods of bleaching, coloring and ornamenting agate and other stones.* AUGUST DREHER.

The claims do not give a clear idea of the process, in which nitric acid, caustic alkali and coloring matters are used alternately.

220,720.—*Manufacture of aluminous cake.* FRANCIS LAUR.

Sulphate of alumina, prepared from bauxite or a similar material, contains more or less iron. The invention consists in the treatment of the solution with metallic zinc; after evaporation, the resulting aluminous cake is not colored by the iron, which has been reduced to the state of protoxide.

220,745.—*Preparation of pepsin.* WM. H. BALL.

A compound of pepsin and salt.

220,825.—*Processes for producing malt extract.* GUSTAVUS A. GESSNER.

In order to avoid fermentation, the extraction is carried on at 156–160° F.

220,872. *Processes of extracting malt in the manufacture of beer.* JOHN A. SCHAEFER.

In a process wherein ground and bolted malt meal is used, and the filtering is done through straw, the clogging of the straw filter is avoided by mixing the malt meal with water of only 95° F. at first, and then raising the temperature gradually to the boiling point.

Reissue 8,943 of patent 206,680.—*Processes of making lead pigments.* GEORGE T. LEWIS.

Claim: The process of manufacturing the basis of a pigment, by subjecting unroasted galena in mass to the simultaneous action of heat and blast, in a furnace capable of oxidizing the sulphuret of lead, and collecting the fumes in textile fabrics.

October 28, 1879.

221,008.—*Pumps for compressing ammoniacal and other gases.* EDGAR G. WHEELER.

221,017.—*Paving compositions.* MICHAEL B. BAILEY.

221,028.—*Compositions for coating metals.* AARON B. and WENDELL P. BROWN.

To prevent rust and corrosion, the metal is coated with a mixture of india-rubber, gum-kauri, gum-dammar and wax; the whole dissolved in benzole.

221,096.—*Concrete pavements.* ANTONIO PELLETIER.

221,113.—*Processes for preserving meats.* CHRISTOPHER C. SMITH.

Brief: The meat is placed in pickle from four to six weeks, removed therefrom and dipped in scalding water, and then coated with a mixture consisting of equal parts of lime, meal and pepper, and laid away on shelves.

221,114—221,120.—*A series of patents for various new coloring matters.* JAMES H STEBBINS, JR.

The reactions by which these coloring matters are obtained are the following: diazobenzole nitrate on pyrogallol, on picric acid, on cresole, on salicylic acid, on naphthalamine, on toluolediamine, and diazonaphthalene nitrate on diamidonaphthalene.

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